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# Selective removal of H<sub>2</sub>S from sour gas with microporous membranes. Part I. Application in a gas–liquid system\*

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## Abstract

The selective removal of H<sub>2</sub>S from gases containing several acidic components by absorption in aqueous alkanolamines is determined by the ratio of the partial mass transfer resistances in the gas and liquid phase and the solubility (physical and chemical) of these gases in the absorption liquid. The influence of the mass transfer resistances is experimentally studied in the present study. The simultaneous absorption of H<sub>2</sub>S and CO<sub>2</sub> in aqueous solutions of methyl-di-ethanol amine (MDEA) was studied in a stirred cell with flat, horizontal microporous wetted or non-wetted membranes which increase the partial mass transfer resistances in the liquid or gas phase, respectively. It was found that non-wetted membranes do not increase the H<sub>2</sub>S flux because the absorption rate determining mass transfer step which is located in the gas phase, is reduced, while the CO<sub>2</sub> transport is not affected significantly. Wetted membranes reduce the transport of the amine to the gas–liquid interface which introduces an additional transport limitation of the amine. Therefore the H<sub>2</sub>S and CO<sub>2</sub> flux are both determined by the mass transfer in the liquid phase which is generally not the case for H<sub>2</sub>S with a gas–liquid interface without a membrane. The introduction of a non-wetted membrane in the gas–liquid interface has no effect on the values of the liquid phase mass transfer coefficients, despite the different hydrodynamic situation at the interface. In this case however, a considerable difference was observed for the gas phase mass transfer coefficients. The influence of physical and chemical solubility is studied in the second part of the present paper in which a liquid membrane of pure MDEA is investigated.

**Keywords** gas separations, microporous and porous membranes, H<sub>2</sub>S/CO<sub>2</sub> selectivity

## Introduction

The removal of H<sub>2</sub>S from industrial gas streams is a very important process because H<sub>2</sub>S is very toxic, highly corrosive, it poisons cata-

lysts and after combustion it is one of the major sources for the environmental problem of acid rain. Therefore nearly all H<sub>2</sub>S must be removed (usually < 4 ppm) before these gases are suitable for application in e.g. process industry or energy generation.

Among other processes, the absorption of H<sub>2</sub>S in a liquid phase is frequently encountered. Usually, a reactive basic component is present in this liquid which reacts with the

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acidic  $\text{H}_2\text{S}$  in order to increase the absorption rate and capacity. Basic components like alkaline and alkanolamines in both aqueous and non-aqueous solutions are often applied (Kohl and Riesenfeld [1]).

In order to minimise the consumption of chemicals, the reaction between  $\text{H}_2\text{S}$  and the basic component must be preferentially reversible in order to be able to regenerate the chemical solvent. In a cyclic process the  $\text{H}_2\text{S}$  is absorbed in the liquid in an absorber. In the desorber the loaded liquid is regenerated producing a lean solvent and concentrated  $\text{H}_2\text{S}$  gas. Next, this  $\text{H}_2\text{S}$  stream can be treated in a so-called Claus unit in which it is converted to elemental sulfur. Aqueous alkanolamine solutions are often used for  $\text{H}_2\text{S}$  treating processes because these components meet all requirements for a cyclic process.

A selectivity problem arises when besides  $\text{H}_2\text{S}$  other acidic gases are present in the mixture. For instance, in many natural gases  $\text{CO}_2$  is present which can also be absorbed in the liquid. If co-absorption of  $\text{CO}_2$  occurs, a larger amount of amine solution has to be used in order to remove  $\text{H}_2\text{S}$  to the desired degree. In the desorber heat must be supplied to regenerate the amines. With a larger solvent flow more steam is needed which increases the treating costs. Moreover, if the desorbed gas contains other components than  $\text{H}_2\text{S}$  a larger Claus plant is required to handle the gas stream which has also a negative effect on the treating costs.

Blauwhoff and Van Swaaij [2] showed that one of the factors which influence the selectivity of the absorption process is the ratio of the mass transfer resistances in gas and liquid phase. In general it can be stated that the  $\text{H}_2\text{S}$  flux for low partial pressures mainly depends on mass transfer in the gas phase while the  $\text{CO}_2$  flux is determined by mass transfer and chemical reaction in the liquid phase.

The ratio of the mass transfer resistances is among others dependent on the hydrodynam-

ics of the reactor in which the process is carried out. Therefore the selectivity of the  $\text{H}_2\text{S}$  removal can be manipulated by the selection of the gas-liquid reactor. However, the turndown ratio of tray columns and packed beds is usually restricted and thus the variation of the ratio of  $k_G$  and  $k_L$  is usually very limited. A lot of research effort was invested in new types of reactors as the centrifugal reactor (Versteeg and van Swaaij [3]) and the cyclone reactor (Schrauwen and Thoenes [4]) in order to improve the  $k_G/k_L$  ratio and therefore the selectivity. A comparison of the  $\text{H}_2\text{S}$  selectivities obtained among others with these reactors to those observed in traditional reactors is presented by Bosch et al. [5].

The present study is part of a research project in which membranes are used to create a fixed gas-liquid interface. Owing to the large specific areas that can be obtained in membrane modules this may result in a compact gas-liquid reactor. Microporous membranes are preferred to ultrafiltration, reverse osmosis or permselective membranes because of their large porosities and pore diameters which lead to substantially higher fluxes. When membranes are used in the hollow fibre form the specific interfacial area of the membrane reactor is inversely proportional to the membrane diameter, e.g. with a membrane diameter of  $10^{-3}$  m the specific area is about  $3000 \text{ m}^2/\text{m}^3$ . Compared to conventional reactors with areas between  $500\text{--}1000 \text{ m}^2/\text{m}^3$  (van Landegem [6]) a substantial increase of the specific area can be achieved by using hollow fibre membrane modules as gas-liquid contactors.

Besides the substantial increase of the interfacial area it may also be possible to improve the selectivity of the  $\text{H}_2\text{S}$  removal by means of these microporous membranes, which is the subject of this study. It is made up of two parts. In the first part the mass transfer resistance in gas or liquid phase is increased by choosing either non-wetted or wetted microporous mem-

branes, respectively. In this way the  $k_G/k_L$  ratio can be affected and therefore the  $H_2S$  selectivity of the absorption process.

Contrary to the generally applied aqueous alkanolamines as used in part I of this study, part II is concerned with selective  $H_2S$  removal by a pure alkanolamine. In these liquids the physical and chemical solubility of  $CO_2$  and  $H_2S$  can positively influence  $H_2S$  selectivity. Because of their high viscosities these liquids cannot be used in conventional gas-liquid absorption processes. However it is possible to use them as a supported liquid membrane which means that a microporous membrane is impregnated with the  $H_2S$  selective liquid.

## Theory

Selectivity between  $H_2S$  and  $CO_2$  in gas absorption processes has been subject of research for a long time. Three factors are identified which influence this selectivity when aqueous solutions of alkanolamines are used as an absorption liquid (Blauwhoff and Van Swaaij [2]).

- (1) Mass transfer resistances determined by the hydrodynamics of the reactor configuration.
- (2) Reaction rate of the transferred components in the reactive fluid
- (3) Chemical and physical equilibria of  $CO_2$  and  $H_2S$  in the amine solution.

Owing to the usually large differences in driving force between  $H_2S$  and  $CO_2$  the ratio of the fluxes is not an illustrative measure for the selectivity. A more suitable definition of selectivity is given in eqn. (1) in which the fluxes are compensated for the concentration differences

$$S = \frac{J_{H_2S} / \left( [H_2S]_G - \frac{[H_2S]_L}{m_{H_2S}} \right)}{J_{CO_2} / \left( [CO_2]_G - \frac{[CO_2]_L}{m_{CO_2}} \right)}$$

$$= \frac{K_{G,H_2S}}{K_{G,CO_2}} = \frac{\left( \frac{1}{k_G} + \frac{1}{mk_L E} \right)_{CO_2}}{\left( \frac{1}{k_G} + \frac{1}{mk_L E} \right)_{H_2S}} \quad (1)$$

In this equation the three factors mentioned above are incorporated. The sensibility of selectivity for the mass transfer coefficients for the gas and the liquid phase is straightforward but in the evaluation of the enhancement factor,  $E$ , the reaction rates, the chemical equilibrium and the mass transfer in the liquid phase must be considered. The enhancement factor  $E$  is the ratio of the fluxes obtained with and without chemical reaction when the same concentration differences are applied.

The reaction rate of  $H_2S$  with the aqueous solutions of alkanolamines can be considered as instantaneous with respect to mass transfer, while the reaction rate of  $CO_2$  in these solutions decreases considerably going from primary to secondary to tertiary amines. The influence of the chemical equilibrium must be taken into account for both reactions because it determines the maximum loading capacity of the liquid.

For high concentrations of  $H_2S$  in the gas phase the absorption is mainly determined by mass transfer and chemical reaction in the liquid phase. However, for low gas phase concentrations of  $H_2S$  (ppm range) the mass transfer of  $H_2S$  is mainly determined by the transport in the gas phase. The absorption of  $CO_2$  usually remains determined by the reaction and mass transfer in the liquid phase, independent of the  $CO_2$  concentration level. Therefore the mass transfer in the gas phase must be increased or the mass transfer of  $CO_2$  in the liquid phase must be decreased to obtain a higher  $H_2S$  selectivity.

Versteeg et al. [7,8] and Bosch et al. [5] developed numerical models in which the three factors mentioned above are incorporated for

absorption processes with complex reversible reactions. This model was used to show the dependency of the selectivity (eqn 1) on  $k_G$  and  $k_L$  for an aqueous solution of the tertiary alkanolamine methy-diethanolamine (MDEA) (Fig 1 and Table 1), which is frequently used in industry.

Figure 1 shows that selectivity goes through a maximum (for a given  $k_G$ ) when  $k_L$  is increased. Low selectivities are obtained at small  $k_L$  values because the reaction rates for both gases with the amine are instantaneous compared to the mass transfer in this region. Therefore both  $\text{CO}_2$  and  $\text{H}_2\text{S}$  fluxes are determined by the transport in the liquid phase and the enhancement factor is equal to the maximum attainable value,  $E_\infty$  (Westertorp et al. [9])

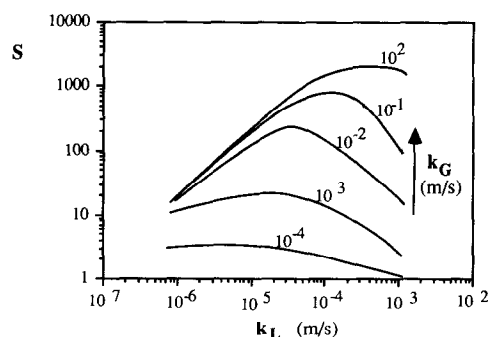


Fig 1 Selectivity as defined by eqn (1) for the selective removal of  $\text{H}_2\text{S}$  from a mixture with  $\text{CO}_2$  by a 2 M MDEA solution as a function of liquid and gas phase mass transfer coefficient (data in Table 1)

TABLE 1

Conditions for the calculated selectivity factor in  $\text{H}_2\text{S}/\text{CO}_2$  removal (Fig 1)

$T$	298 K
$k_{\text{CO}_2\text{MDEA}}$	$4.5 \times 10^{-3} \text{ m}^3/\text{mol}\cdot\text{sec}$
$C_{\text{CO}_2\text{G}}$	$3 \text{ mol}/\text{m}^3$
$C_{\text{H}_2\text{S G}}$	$0.01 \text{ mol}/\text{m}^3$
$C_{\text{MDEA L}}$	$2000 \text{ mol}/\text{m}^3$
Bulk $\text{H}_2\text{S}$ loading of the amine	1%
Bulk $\text{CO}_2$ loading of the amine	1%

At high  $k_L$  values the mass transfer resistance of the liquid phase for both gases is negligible to the mass transfer resistance of the gas phase.  $\text{CO}_2$  and  $\text{H}_2\text{S}$  transport is determined by the mass transfer in the gas phase which results in low selectivities as well. In the intermediate  $k_L$  region the influence of the reaction rate becomes important. For  $\text{H}_2\text{S}$  the mass transfer resistance in the liquid is reduced substantially by its reaction with the amine which is not the case for the reaction rate of  $\text{CO}_2$  with the amine. Therefore the overall mass transfer resistance for  $\text{CO}_2$  is larger than for  $\text{H}_2\text{S}$  which gives a high  $\text{H}_2\text{S}$  selectivity as defined by eqn (1). The process of simultaneous absorption of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  becomes complex if higher concentrations of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  occur. The amine in the mass transfer film becomes depleted. Blauwhoff and Van Swaaij [2] studied these phenomena and defined three regimes with an increasing amine depletion at the interface: negligible, intermediate and the extreme interaction regime. In this last regime desorption can occur although absorption is expected on basis of the overall driving force. With a relatively high absorption flux of one of the gas components the reaction of the other gas component with the amine can be reversed which results in desorption of this component.

For the negligible interaction regime, eqn. (1) can be simplified. It is assumed that the transport of  $\text{H}_2\text{S}$  is only determined by mass transfer in the gas phase, which gives:

$$S = \frac{k_{G,\text{H}_2\text{S}}}{k_{G,\text{CO}_2}} + \frac{k_{G,\text{H}_2\text{S}}}{(mk_L E)_{\text{CO}_2}} \cong 1 + \frac{k_{G,\text{H}_2\text{S}}}{(mk_L E)_{\text{CO}_2}} \quad (2)$$

A higher selectivity is simply obtained by increasing the  $k_G/k_L$  ratio if the absorption takes place in the negligible interaction regime. In the present study porous membranes are introduced at the gas-liquid interface which offer the possibility of manipulating the  $k_G/k_L$  ratio. Either wetted or non-wetted membranes can be chosen which increases the mass transfer resis-

tance in the liquid or the gas phase, respectively

With a non-wetted membrane a stagnant gas layer is present in the pores. This layer results in an additional mass transfer resistance ( $1/k_M$ ) next to the overall mass transfer resistance in the gas and liquid outside the membrane, eqn (3)

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k_M} + \frac{1}{mk_L E} \quad (3)$$

$k_M$  can be calculated according to eqn (4) (Kreulen et al. [10]).

$$k_M = \frac{D_G \epsilon}{d_M \tau} \quad (4)$$

In microporous membranes the diffusion process is determined by the mechanisms of continuum and Knudsen diffusion. Effectively the mass transfer in the gas phase is reduced. If the mass transfer parameter for the liquid phase is not affected by the membrane this type of membrane does not increase  $H_2S$  selectivity

A wetted membrane may increase selectivity because the ratio of mass transfer resistances in the gas and the liquid (including the membrane) is changed. The mass transfer in the liquid is reduced by the additional membrane resistance  $1/(mk_M E_M)$  in eqn. (5)

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{mk_M E_M} + \frac{1}{mk_L E_L} \quad (5)$$

$k_M$  can be calculated with eqn (4) if instead of the gas diffusion coefficient, the liquid phase diffusion coefficient is used. In eqn. (5) enhancement factors should be distinguished for the membrane and the liquid because in these two phases the interaction of mass transfer and chemical reaction is different. In the liquid phase also convection determines the mass transfer while in the membrane only diffusion is the mechanism for mass transfer

The partial mass transfer coefficients in eqns. (3) and (5) can be measured in an absorption system without chemical reaction. It should be

realised that the hydrodynamics at the fixed membrane interface differ from an interface with a freely moving gas/liquid interface. This could also result in a difference in the mass transfer at these interfaces. However, Kreulen et al. [10] did not observe a significant difference between the liquid phase mass transfer parameters measured in a system with and without a non-wetted membrane in an interface

## Experimental

The simultaneous absorption of  $H_2S$  and  $CO_2$  was studied in a stirred cell with a horizontal gas–liquid interface. In Fig. 2 a schematic drawing of this set-up is presented. In the stirred cell which was operated at 298 K a flat membrane could be placed at the interface between the gas and liquid phase. The volume of each compartment was  $5 \times 10^{-4} \text{ m}^3$ . On both stirring axes 4 stirrers with 4 blades were mounted. The stirrers were magnetically driven. The absorption liquid (2.0 M MDEA) was pumped from a storage vessel through the cell into a communicating vessel with which the liquid level in the cell was controlled. The loaded amine solution was regenerated in a stripper. The absorbed components were released from the boiling liquid and removed by a nitrogen stream while the liquid was recycled to the storage vessel. Effluent  $H_2S$  from the reactor and the stripper was absorbed in a sodium hydroxide solution in a countercurrently operated packed bed.

The gas phase was operated at atmospheric pressure.  $H_2S$  and  $CO_2$  were used as absorbing gases while  $N_2$  was used as an inert carrier gas.  $N_2O$  was used in physical absorption measurements. Because of the analogy in solubility and diffusion coefficient of  $CO_2$  and  $N_2O$  (Laddha et al. [11]) accurate estimates can be made for

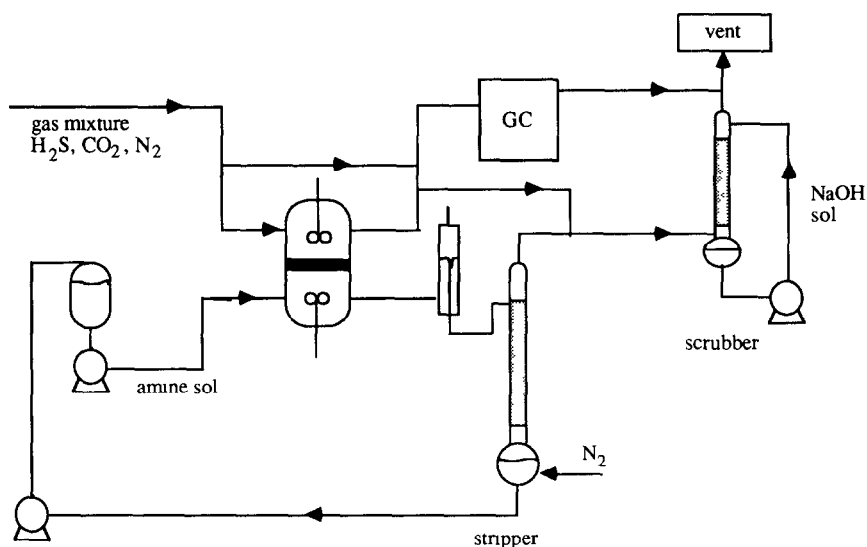


Fig 2 Experimental set-up

the physical absorption of  $\text{CO}_2$  in the amine solution.

From the absorption of  $\text{H}_2\text{S}$  in the amine solution through a wetted membrane physical mass transfer parameters can be obtained although the absorption is accompanied by a chemical reaction. Therefore the approach of Olander [12] was followed and worked out for the special case of a wetted membrane in contact with a stirred liquid. The two-film concept for mass transfer and chemical equilibrium reaction (Kreulen et al [10]).

Fluxes were calculated from the concentrations and flows of the gas phase. Gas concentrations were determined by a gas chromatograph, Varian 3400, equipped with a thermal conductivity detector (TCD) and a flame photometric detector (FPD). Gas flows were measured with a soap-film meter.

Mass transfer parameters in three different systems were measured:

- (1) Gas-liquid interface with no membrane
- (2) Gas-liquid interface with a non-wetted membrane
- (3) Gas-liquid interface with a wetted membrane

The non-wetted membranes were supplied by AKZO (Accurel, polypropylene) with average pore diameters of 0.1 and 0.2  $\mu\text{m}$ , thickness 145  $\mu\text{m}$  and porosity 70-75%. Wetted membranes were purchased from Pall (nylon-66), average pore diameter 0.1  $\mu\text{m}$ , thickness 100  $\mu\text{m}$ , porosity 70%. Both types of membranes were glued between metal rings to give an interfacial area of  $30 \times 10^{-4} \text{ m}^2$ .

For non-wetted membranes special attention must be paid to the contact between the liquid and the membrane. This could be realised by placing the liquid level in the communicating vessel a few millimeters higher than the membrane itself. Because of this small overpressure, liquid was in good contact with the membrane, which was checked visually. The material of the membrane prevents the liquid entering the pores of the membrane.

For wetted membranes care had to be taken to avoid the presence of a liquid layer on the membrane in the gas phase. Therefore at the beginning of the experiments the liquid level in the communicating vessel was set higher than the membrane. In this way it was ascertained that the membrane was filled with liquid which

was visually observed by a distinct colour change of the membrane. Next the liquid level in the communicating vessel was lowered a few millimeters under the membrane and consequently the liquid level in the cell lowered. Owing to capillary forces the liquid was kept in the membrane without an additional liquid layer on top of the membrane.

## Results

### Gas phase mass transfer

Gas phase mass transfer coefficients were measured using very diluted  $\text{H}_2\text{S}$  (<2000 ppm at inlet) in nitrogen. The  $\text{H}_2\text{S}$  concentrations were chosen such that mass transfer resistances for the  $\text{H}_2\text{S}$  transport in the liquid phase could be neglected (Danckwerts [13]).

To check whether any mass transfer resistance was present in the liquid phase the liquid stirrer speed was increased. No influence could be detected for the systems without a membrane and the system with a non-wetted membrane. Therefore it was concluded that the mass transfer coefficients measured in these cases are not affected by a mass transfer resistance in the liquid.

The experimental results of the measured  $K_G$  values for the three systems are presented in Fig 3(a,b) for non-wetted and wetted membranes, respectively. The upper line in Fig 3(a) represents the mass transfer coefficients measured with a free gas/liquid interface,  $K_G/N^{0.78}$ . A similar dependency (0.63) is reported by Versteeg et al [14] from experiments also carried out in a stirred cell.

The experimental values for the non-wetted membrane are smaller than for the free interface. This can be attributed to the stagnant gas layer present in the pores of the membrane.

With the aid of eqn (4), derived in an earlier study (Kreulen et al [10]) it is possible to estimate the mass transfer resistance of the stagnant membrane. With the membrane thickness ( $145\text{ }\mu\text{m}$ ), the porosity/tortuosity factor (0.2), Knudsen diffusion coefficient of  $\text{H}_2\text{S}$  in the pores of the membranes ( $5.7 \times 10^{-5}\text{ m}^2/\text{sec}$ ) and the binary diffusion coefficient of  $\text{H}_2\text{S}$  in  $\text{N}_2$  ( $1.8 \times 10^{-5}\text{ m}^2/\text{sec}$ ),  $k_M$  is equal to  $1.9 \times 10^{-2}\text{ m/sec}$ . Next, eqn (3) can be used to calculate the partial gas phase mass transfer coefficient from the experimental data. The result is presented in Fig 3(a) as the drawn line in the middle of the lines for the experimental points. For low stirrer speeds the membrane resistance can be neglected compared to the mass transfer resistance in the gas phase layer above the membrane. Increasing the stirrer speed shows a relative increase of the mass transfer resistance of the membrane. However, the partial membrane mass transfer coefficients for the gas phase above the moving and the fixed gas/liquid interface are not equal which indicates that the hydrodynamic situation at these two interfaces is different.

In the case of a wetted membrane an influence of the liquid stirrer speed could not be detected on the measured mass transfer coefficients (see Fig. 3b). However, it is clear that another mass transfer resistance, apart from that of the gas phase, is present because the experimental values of  $K_G$  are significantly lower than those of the two systems presented in Fig. 3(a).

With the two-film concept (Kreulen et al [10]) the  $\text{H}_2\text{S}$  concentration at the gas-membrane interface can be obtained. These calculations show that the mass transfer of  $\text{H}_2\text{S}$  is also influenced by the wetted membrane which accounts for 15 to 6% of the mass transfer resistance between the lowest and the highest gas phase stirrer speed.

From the measured fluxes and the calculated interface concentrations the partial mass



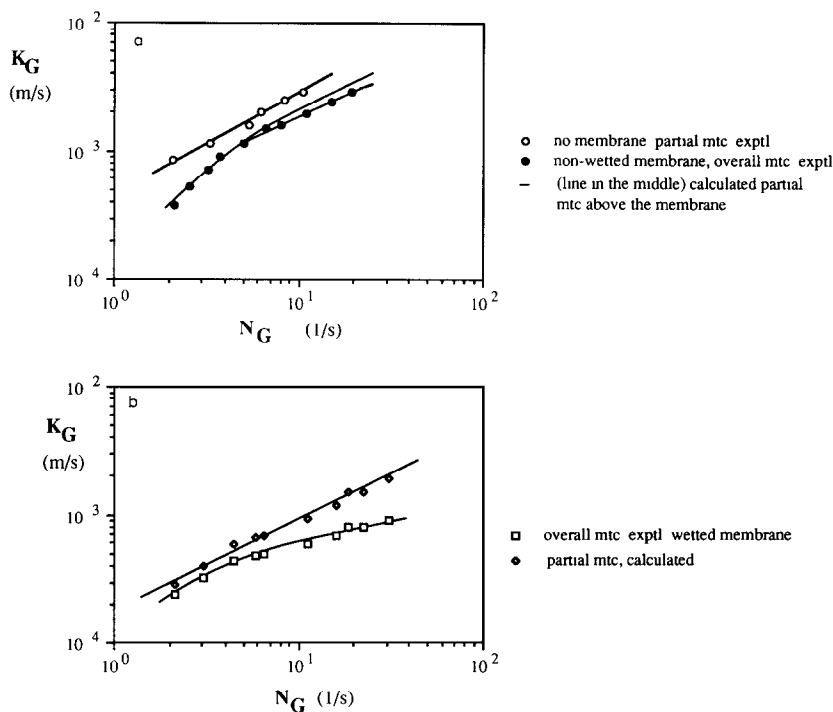


Fig 3 (a) Gas phase mass transfer coefficient (mtc) as function of the gas phase stirrer speed for two different systems Absorption of  $\text{H}_2\text{S}$  in an aqueous 2.0 M MDEA solution at 25°C and atmospheric pressure (b) Gas phase mass transfer coefficient (mtc) as function of the gas phase stirrer speed Absorption of  $\text{H}_2\text{S}$  in an aqueous 2.0 M MDEA solution at 25°C and atmospheric pressure

transfer coefficients for the gas phase can be calculated (see Fig. 3b). Still these values are significantly lower than the  $K_G$  values for the free gas–liquid interface. As for the experiments with the non-wetted membranes it must be concluded that similar to the conclusion presented before a difference exists between the mass transfer in the gas phase at a fixed and a free gas–liquid interface.

The experimentally determined  $K_G$  values for the wetted membrane tend to reach a limit at higher stirrer speeds. The mass transfer resistance in the gas phase becomes negligible and thus the flux is determined by the resistances in the membrane and the liquid under the membrane. This maximum  $K_G$  value can also be calculated with the two-film concept (Kreulen et al. [10]) in an iterative calculation. A

concentration at the gas–membrane interface is assumed from which the flux and the overall mass transfer coefficient are calculated. From the mass balance over the gas phase (including the in- and outlet flow) a new outlet concentration (= interface concentration) is calculated. This procedure converges to the limiting  $K_G$  value of  $2.5 \times 10^{-3}$  m/sec in this specific experimental set-up. Considering the small increase of the  $K_G$  values, the maximum value would only be reached at very high stirrer speeds.

#### Liquid phase mass transfer

The experiments to measure the liquid phase mass transfer coefficients were carried out with pure gases to avoid a mass transfer limitation in the gas phase. The results are presented in

Fig 4 For the systems with no membrane and a non-wetted membrane the inert  $N_2O$  was used. No clear difference can be observed between the values measured with these systems. The difference between the fixed and moving gas–liquid interface does not seem to influence the absolute value of the liquid phase mass transfer coefficients.

For the system with no membrane the stirrer speed could not be increased further than  $1.0 \text{ sec}^{-1}$ . At higher stirrer speeds the flat interface was disturbed and therefore the exchanging area is influenced. With a non-wetted membrane higher stirrer speeds could be applied because in this case the exchanging area is fixed by the membrane resulting in larger  $k_L$  values.

The determination of the mass transfer coefficient of the wetted membrane was not possible by means of  $N_2O$  absorption because the rate was too low to be measured accurately. Therefore pure  $H_2S$  was taken instead of  $N_2O$ . Although this gas reacts with the amine present in the liquid,  $K_L$  can be estimated from the experiments with the two-film concept for mass transfer and chemical equilibrium reaction (Kreulen et al. [10]).

The results (Fig 4) show that mass transfer is mainly determined by the stagnant layer in the membrane, with a slight increase with the liquid stirrer speed. The mass transfer coefficient

of the membrane predicted by the film theory, eqn (4) with  $D_L$  instead of  $D_G$ , is in close agreement with the measured values,  $2 \times 10^{-6} \text{ m/sec}$ , based on a porosity of 70% and a tortuosity factor of 4. This value was also found in a previous study (Kreulen et al. [10]).

### Selectivity

A non-wetted membrane reduces the mass transfer rate because of its additional mass transfer resistance in the gas phase which was shown in Fig 3(a). From Fig 4 it can be concluded that  $k_L$  is not reduced by the introduction of a non-wetted membrane. According to eqn (1) the combination of these two effects will negatively influence selectivity and is therefore not of any practical interest to improve on the selective  $H_2S$  removal (see also Fig 1).

For the wetted membrane it is difficult to present a straightforward conclusion from Figs 3 and 4. These results show a decrease of both  $K_L$  and  $K_G$ . This means that the mass transfer rate through a wetted membrane is reduced compared to a free gas–liquid interface. However, owing to the substantial increase of the interfacial areas of hollow fibre membranes this effect can be sufficiently compensated. The exact values of the partial mass transfer coefficient

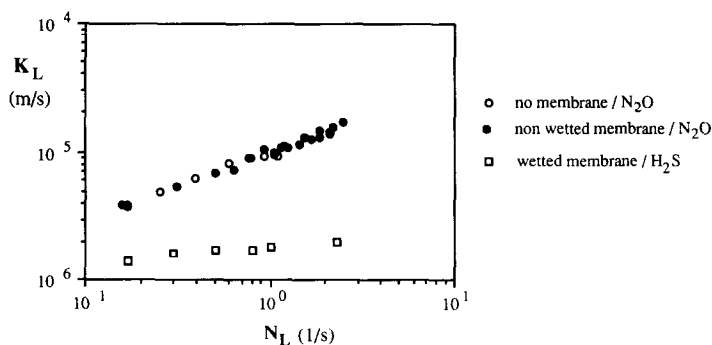


Fig 4 Overall liquid phase mass transfer coefficients as function of the liquid phase stirrer speed for three different systems. Absorption of pure  $N_2O$  and pure  $H_2S$  in an aqueous 2.0 M MDEA solution at 25°C and atmospheric pressure.

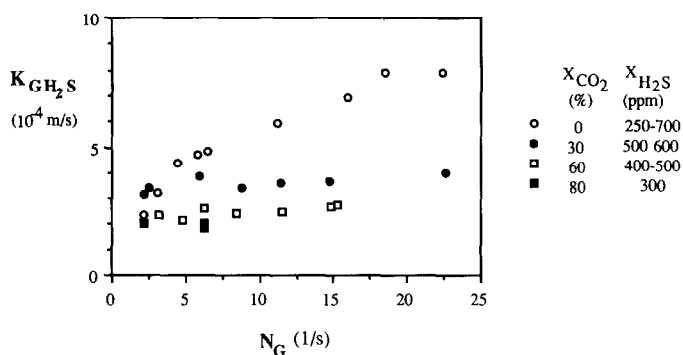


Fig 5 Overall gas phase mass transfer coefficients as function of the gas phase stirrer speed for  $\text{H}_2\text{S}$  transferred from a mixture with different  $\text{CO}_2$  gas fractions through a wetted membrane in an aqueous 2.0 M MDEA solution at 25°C and atmospheric pressure

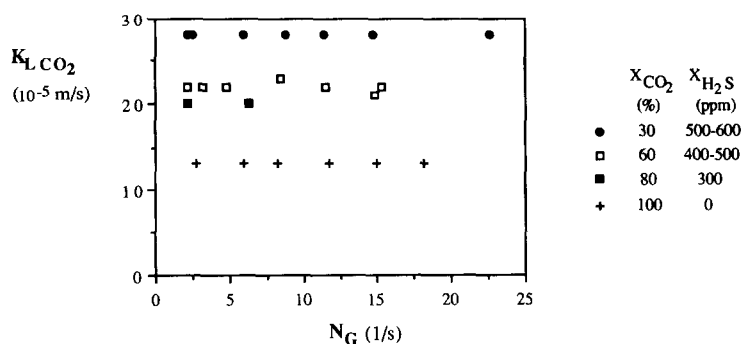


Fig 6 Overall gas phase mass transfer coefficients as function of the gas phase stirrer speed for  $\text{CO}_2$  transferred from a mixture with  $\text{H}_2\text{S}$  through a wetted membrane in an aqueous 2.0 M MDEA solution at 25°C and atmospheric pressure

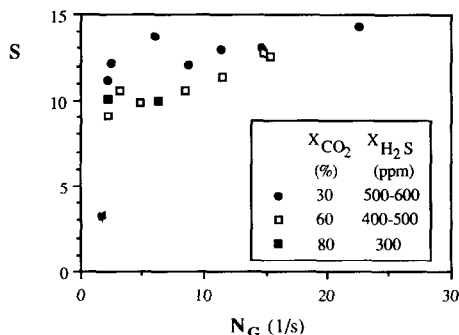


Fig 7 Selectivity as defined by eqn (1) as function of the gas phase stirrer speed, for the simultaneous absorption of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  through a wetted membrane in an aqueous 2.0 M MDEA solution at 25°C and atmospheric pressure

cients cannot be deduced directly from the  $K_L$  and  $K_G$  values to predict whether the  $k_L/k_G$  ratio will decrease to give an increased selectivity. Therefore selectivity is studied experimentally for this type of membrane.

Several experiments were performed with simultaneous absorption of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . The absorption fluxes were determined as a function of the stirrer speed in the gas phase and the gas phase concentrations of  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . The overall mass transfer coefficient, calculated from the experiments is plotted in Fig. 5 with the  $\text{CO}_2$  partial pressure as a parameter. From this figure it can be concluded that the co-absorption of  $\text{CO}_2$  has a negative effect on the mass transfer of  $\text{H}_2\text{S}$ . The interface con-

centration of the amine is lower compared to the situation without  $\text{CO}_2$  because of the reaction of amine with  $\text{CO}_2$ . This implies that the mass transfer of  $\text{H}_2\text{S}$  becomes more determined by the resistance in the liquid phase when the  $\text{CO}_2$  partial pressure is increased.

The influence of the  $\text{CO}_2$  concentration on the mass transfer of  $\text{CO}_2$  in these experiments is presented in Fig. 6. The experiments without  $\text{H}_2\text{S}$  give the same results which indicates that the absorption of  $\text{CO}_2$  is not influenced by the absorption of  $\text{H}_2\text{S}$  at the present concentration level.

With an increase of the  $\text{CO}_2$  partial pressure the overall mass transfer coefficient becomes smaller. This indicates that the flux of  $\text{CO}_2$  becomes more determined by diffusion of MDEA at higher partial pressures. For the completely diffusion controlled regime the mass transfer coefficient is inversely proportional to the partial pressure of  $\text{CO}_2$ . If the reaction rate or the mass transfer were determining the flux the overall mass transfer coefficient of  $\text{CO}_2$  should not be a function of the  $\text{CO}_2$  partial pressure.

In terms of the interaction regimes defined by Blauwhoff and van Swaaij [2] the absorption through the wetted membrane should be characterised as absorption in the intermediate interaction regime. Therefore eqn (2) is not valid for expressing selectivity as a function of  $k_L$  and  $k_G$ .

The absolute values of the experimentally determined selectivity (see Fig. 7) are relatively low if they are compared to the values obtained by Bosch et al. [15]. These authors obtained a selectivity of around 70 in a system without a membrane at the interface while the experimental conditions are similar to the present system.

## Conclusions

In the present study the influence of microporous membranes placed in the gas/liquid in-

terface on the selective removal of  $\text{H}_2\text{S}$  was investigated. Non-wetted membranes are not suitable for this purpose since they decrease the mass transfer of  $\text{H}_2\text{S}$  in the gas phase while the  $\text{CO}_2$  transport is not influenced. Wetted membranes as applied in the present study do not increase  $\text{H}_2\text{S}$  selectivity compared to a system with an interface without a membrane. Owing to the thickness of the membrane, the  $\text{CO}_2$  and the  $\text{H}_2\text{S}$  transport is determined by diffusion of the amine. Therefore the interface concentration of the amine is considerably lower than in the bulk of the liquid phase.

To use the possible selectivity of tertiary amines, however, the  $\text{CO}_2$  transport should be determined by the reaction rate and the  $\text{H}_2\text{S}$  transport should be determined by the mass transfer in the gas phase. With a thinner membrane it may be possible to create this situation. However, the mechanical strength of such a membrane is expected to create problems in practical applications.

Another complication for the practical application of wetted membranes as hollow fibres, is the fact that they cannot keep gas and liquid separated on either side of the membrane. The flat membranes used in the present study could be operated with the help of gravity. To prevent liquid flowing through the membrane wall into the gas phase a very thin non-wetted layer should be applied on the gas side of the membrane. The thickness of this layer should not decrease the mass transfer rates too much because this would reduce the absorption capacity again.

It was found that a difference exists between the gas phase mass transfer at a freely moving and a fixed gas-liquid interface. No difference between a fixed and a moving gas-liquid interface was observed from absorption experiments in which mass transfer in the liquid phase is rate determining. Non-wetted membranes can be applied when large  $k_L$  values are required in a gas-liquid system with a known ex-

change area The turbulence of the stirrer does not influence the flat interface

### List of symbols

$C$	concentration ( $\text{mol}/\text{m}^3$ )
$d$	membrane thickness (m)
$D$	diffusion coefficient ( $\text{m}^2/\text{sec}$ )
$E$	chemical enhancement factor ( $J_{\text{chem}}/J_{\text{phys}}$ ) (-)
$J$	flux ( $\text{mol}/\text{m}^2\text{-sec}$ )
$K$	overall mass transfer coefficient (m/sec)
$k_i$	partial mass transfer coefficient (m/sec)
$k_{i,j}$	second order reaction rate constant ( $\text{m}^3/\text{mol}\text{-sec}$ )
$m$	distribution coefficient ( $C^L/C_G$ ) (-)
$N$	stirrer speed (1/sec)
$S$	selectivity defined by eqn (1) (-)
$X$	fraction (-, %, ppm)
$\epsilon$	membrane porosity (-)
$\tau$	membrane tortuosity (-)

### Indices

G	gas phase
L	liquid phase
M	membrane phase

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